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Analysis of the absorption spectrum of ruby at high pressures

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It is shown that at high pressures, results of absorption measurements are inconsistent with R-line fluorescence data. The observed constancy of R_1 - R_2 splitting under hydrostatic conditions is supported by crystal field analysis. The present findings suggest the need for absorption measurements in ruby crystals under better defined stress conditions.

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Ruby spectra have been the subject of numerous experimental and theoretical investigations due to the utility of ruby as a laser material and as a high pressure sensor in diamond anvil cell studies.¹⁻⁷ At ambient conditions, various details of the spectrum consisting of multiplets of R, R' and B lines, and U and Y absorption bands can be quantitatively understood with symmetry based crystal field theory approach.^{5,8-10} Significant crystal field parameters for description of ruby spectrum turn out to be the following:⁵ Racah parameters B and C, representing electron-electron repulsion of d-electrons of Cr^{3+} ; 10 Dq, characterizing the strength of crystal field of octahedral symmetry; V_{trigonal} , the crystal field of only C_3 symmetry which is the local site symmetry around Cr^{3+} in the corundum lattice.¹¹⁻¹³ The trigonal field is characterized by the magnitude of two matrix elements of this field (between the bases of symmetry adapted sets $\{t_{2g}\}$ and $\{e_g\}$) namely $v = -3 \langle t_{2g} x_+ | V_{\text{trig}} | t_{2g} x_+ \rangle$ and $v' = \langle t_{2g} x_+ | V_{\text{trig}} | e_g u_+ \rangle$, as defined by Pryce and Runciman.¹⁴ Fine multiplet structure of energy levels emerges from the simultaneous presence of trigonal field and spin-orbit interaction and can be explained quantitatively.^{5,8,9}

Attempts to understand variations in ruby spectrum due to hydrostatic pressure, in terms of crystal field approach, have aimed at broad correlations.^{15,16} The fine multiplet structure of lines and bands is completely ignored — thereby approximating the crystal field to have octahedral symmetry only. Variations in crystal field parameters, in the assumed octahedral symmetry, are represented by two independent 'scale parameters',^{15,16} which are determined by the best fit to appropriately averaged experimental data. Such a procedure, by its very nature, overemphasizes the consistency of pressure dependent changes in the spectrum. For example, over 80 percent of the measured shift of the Y band (representing ${}^4T_1 \rightarrow {}^4A_2$ transition) is due to changes in 10 Dq and, therefore, a considerable variation in the pressure dependence of Racah parameters with pressure will not impair the quality of agreement.

In this communication we analyze the consistency between the pressure variation of the absorption bands,¹⁷ and R_1 , R_2 lines¹⁸ in detail i.e. beyond the octahedral approximation in the



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crystal field analysis. The consistency analysis is restricted to this part of the spectrum for two reasons. First, no other lines have such a well defined spectrum as R-lines;¹⁹ second, this restricted analysis suggests the need for experimental measurements of the absorption bands under well characterized conditions of stress, and with improved statistical precision. An accurate determination of the details of the ruby spectrum at high pressure would permit a detailed crystal field analysis similar to that performed by Macfarlane⁹ at ambient conditions.

The results describing the pressure variation of the absorption spectrum, which enter as input to our calculation, have been taken from the polarized light absorption measurements of Stephens and Drickamer.¹⁷ They measured the absorption bands up to 120 kbar and used a crystal field description to derive $10 Dq$, B and trigonal field as a function of pressure. These authors assumed that both the bands viz $U (^4T_2)$ and $Y (^4T_1)$ split by the same amount $\nu/2$. Subsequent analysis of Macfarlane⁹ showed that the splitting of Y band is given by $\frac{\nu}{2} + \nu'$. Hence, only the experimental results of $U (^4T_2)$ band should be used to estimate changes in trigonal field. Further, by comparing the splitting of U and Y bands, we conclude, that variation in ν' with pressure, within experimental errors, is zero. The observed variations of absorption bands from Ref. 17 are summarized as follows, (i) Racah parameter, B , decreases as $.205 \text{ cm}^{-1}/\text{kbar}$ (ii) $10 Dq$ increases at a rate, $10.9 \text{ cm}^{-1}/\text{kbar}$ (iii) trigonal field parameter ν shows little or no change up to $\approx 75 \text{ kbar}$, beyond which it increases rapidly. We now use these results to calculate the variations in R_1 , R_2 lines with pressure. The calculation of the red shift is followed by the calculation for R-lines splitting.

Reduction in Racah parameter B with pressure implies a red shift of the R lines and is, therefore, in qualitative agreement with experimental observations.¹⁸ If there is no change in the trigonal field with pressure, then the rate of the red shift with pressure can be deduced by diagonalizing the 4×4 matrix representing Coulomb interaction.⁵ With the above mentioned observed values,¹⁷ the red shift of R lines is given by $4.26 \text{ cm}^{-1}/\text{kbar}$ [Assume $C/B = 5.1245$ to get position of R lines

at ambient conditions]. This is to be compared with the measured¹⁸ red shift of .76025 cm⁻¹/kbar; this is smaller by a factor of five when compared to the calculated shift. A calculation based on sensitivity analysis, after Macfarlane,⁹ which includes configuration interaction, confirms that the calculated red shift is about a factor of five larger than the observed value. This implies that the variation of Racah parameter, obtained from absorption experiments, is in significant disagreement with the red shift of R lines.

As pointed out earlier, coexistence of the trigonal field and spin-orbit interaction bring about splitting of ²E giving rise to the, R₁, R₂ lines. Within second order perturbation theory, the splitting between R₁, R₂ lines can be written as

$$\Delta(R_1 - R_2) = \frac{\frac{4}{3} v \zeta}{\epsilon(^2T_2) - \epsilon(^2E)} \quad (1)$$

where ζ represents the strength of the spin-orbit interaction. Eq. (1) can be used to predict the change in splitting with changes in the trigonal field. We shall assume that spin-orbit interaction does not change with pressure — an approximation that is consistent with an analysis of the lifetime variation of R₁ line with pressure.²⁰ Alternatively, we can use the following result due to Macfarlane²¹ to evaluate the changes in R-line splitting due to variations in the trigonal field

$$\Delta(R_1 - R_2) = D_o - 0.027 v_p - 0.008 v_{p'} \quad (2)$$

Here, D_o represents splitting at $P=0$, and v_p and $v_{p'}$ are pressure dependent changes in v and v' . For the same input, Eq. (1) gives a larger splitting than Eq. (2) and so we term the results of Eq. (1) as upper and that of Eq. (2) as lower bound. In principle Eq. (2) should be more accurate, as it includes configuration interaction. We have used both equations because experimental results¹⁹ of relative movements of R and R' lines do not confirm the predictions of Macfarlane's calculation.⁹

We now calculate the R-line splitting due to the trigonal field changes, reported on the basis of the absorption measurements.¹⁷ We take $\epsilon(^2T_2) - \epsilon(^2E)$ from Ref. 9 and $\zeta = 186.1 \text{ cm}^{-1}$, to reproduce R-line splitting at ambient pressure. Results for a few representative pressures are given in Table I.

Therefore, the absorption data of Stephens and Drickamer¹⁷ imply no change in splitting up to about 75 kbar and then a large change. At 120 kbar, the splitting increases by approximately 30% compared to that at 75 kbar. However, the experimental results for R-lines, consisting of 38 sets of data up to 150 kbar, tested for statistical consistency,¹⁸ are incompatible with the results above 75 kbar. The experimentally observed rate of change of splitting is¹⁸ $.0025 \pm 0.004 \text{ cm}^{-1}/\text{kbar}$. This result implies that within the experimental accuracy, there is no change in splitting up to 150 kbar, in contrast to the results shown in Table I.

Experimental results of R-lines, aside from better precision and mutual statistical compatibility,¹⁸ are also consistent with crystal field analysis as shown below. We use the point ion approximation to estimate changes in the crystal field. Although this approximation is known to be inadequate for calculation of crystal field parameters at ambient conditions,^{10,22} it gives a reasonable estimate of stress induced changes.^{21,23,24}

As the site symmetry of Cr^{3+} site is C_3 , the potential function for an electron can be written³ as

$$\begin{aligned} V = & B_0^0 + B_1^0 r \cos \theta + B_2^0 r^2 (3 \cos^2 \theta - 1) + B_3^0 r^3 (5 \cos^3 \theta - 3 \cos \theta) \\ & + B_3^3 r^3 \sin^3 \theta \cos 3\phi + C_3^3 r^3 \sin^3 \theta \sin 3\phi \\ & + B_4^0 r^4 (35 \cos^4 \theta - 30 \cos^2 \theta + 3) + B_4^3 r^4 \sin^3 \theta \cos \theta \cos 3\phi + \dots \end{aligned} \quad (3)$$

where B_n^m and C_n^m are the lattice sums over real and imaginary part of the functions of the type $\frac{j}{R^{n+1}} Y_{lm}$ as defined and calculated by McClure³ at ambient conditions [the constant j depends on the position of the atom with respect to the symmetry axis and R represents lattice vectors].

The trigonal field parameters v and v' can now be represented in terms of B_n^m as follows^{3,23}

$$v = \frac{6}{7} B_2^0 \langle r^2 \rangle + \frac{160}{63} \left[B_4^0 + \frac{B_4^3}{20\sqrt{2}} \right] \langle r^4 \rangle \quad (4)$$

$$v' = \frac{-2\sqrt{2}}{7} B_2^0 \langle r^2 \rangle + \frac{40\sqrt{2}}{63} \left[B_4^0 + \frac{B_4^3}{20\sqrt{2}} \right] \langle r^4 \rangle \quad (5)$$

We assume that hydrostatic pressure results in an isotropic compression of the rhombohedral cell²⁵⁻²⁸ of ruby and that all interatomic distances change uniformly and proportionally to unit cell dimensions a . This assumption seems to be reasonable up to $\approx 3\%$ compression (≈ 100 kbar).²⁹

Then it can be shown that $\frac{\delta B_n^m}{B_n^m} = (n+1) \frac{\delta a}{a}$ for small $\delta a/a$. Such an approximation gives reasonable agreement with experiments.³⁰ The changes in v and v' under pressure can then be written as follows

$$\delta v = -\frac{\delta a}{a} \left[\frac{18}{7} B_2^0 \langle r^2 \rangle + \frac{800}{63} \langle r^4 \rangle \left[B_4^0 + \frac{B_4^3}{20\sqrt{2}} \right] \right] \quad (6)$$

$$\delta v' = \frac{\delta a}{a} \left[\frac{6\sqrt{2}}{4} \langle r^2 \rangle B_2^0 - \frac{200\sqrt{2}}{63} \langle r^4 \rangle \left[B_4^0 + \frac{B_4^3}{20\sqrt{2}} \right] \right] \quad (7)$$

$$\text{Taking } \langle r^4 \rangle / \langle r^2 \rangle = 3.0732 \quad (8)$$

as estimated by Schawlow et al.,²⁴ from Hartree-Fock solutions for a free Cr^{3+} ion, we get

$$\delta v = \frac{\delta a}{a} \langle r^2 \rangle .101803 \quad (9)$$

$$\delta v' = \frac{-\delta a}{a} \langle r^2 \rangle .256326 \quad (10)$$

Eqs. (9) and (10) give a negative δv and a positive $\delta v'$ consistent with earlier conclusions.²¹

Substituting these values in Eq. (2) gives

$$\Delta(R_1 - R_2) = D_0 + 6.981 \times 10^{-4} \langle r^2 \rangle \frac{\delta a}{a}$$

For ruby $\frac{\delta a}{a} = -1.28 \times 10^{-4} P$, where P is pressure in kbar.²⁵⁻²⁷ This gives a splitting of

$$\Delta(R_1 - R_2) = D_0 - C_1 P \quad (12)$$

Where $C_1 = 8.935 \times 10^{-8} \langle r^2 \rangle$ ev/kbar. The value of $\langle r^2 \rangle$ has been estimated to be .4048

A^2 with Hartree-Fock wavefunction and $1.38 A^2$ with Slater's wavefunction by Schawlow et al.²⁴ These give $[C_1]_{HF} = 2.92 \times 10^{-4} \text{ cm}^{-1}/\text{kbar}$ and $[C_1]_{Slater} = 9.95 \times 10^{-4} \text{ cm}^{-1}/\text{kbar}$ implying that the splitting changes at the rate $.001 \text{ cm}^{-1}/\text{kbar}$ or less and is negligible. This finding is consistent with observed results. At compressions larger than 3%, local compressibility around Cr^{3+} may be smaller than the bulk compressibility²⁹ of Al_2O_3 . Then the above analysis would give an upper limit on variation of trigonal field within the point ion approximation.

On the basis of the above analysis, we conclude that the R-line data are consistent with crystal field model. The high pressure, absorption results reported in Ref. 17 are not consistent with R line data, on both counts — the red shift as well as splitting of R_1, R_2 lines; the splitting results are consistent to 75 kbar. We conjecture that the inconsistency between the absorption and the R-line results may arise, in part, due to the possibility of non-hydrostatic stresses. It is known that non-hydrostatic stresses due to either uniaxial stress³¹ or uniaxial strain³² bring about changes in the trigonal field. Hence, the existence of non-hydrostatic stresses beyond 75 kbar in the experimental configuration used in Ref. 17 may explain the increase in the trigonal field. Experimental data are needed to verify this conjecture. In addition, to accurately determine the adequacy of the crystal field description for modeling ruby spectrum at high pressures, there is a need for high precision absorption data under well defined hydrostatic pressures.

Before concluding, we would like to make another observation. Ma et al.¹⁶ assume an effective interaction between 2E and 2T_1 states which is an increasing function of trigonal field. To explain the experimental observations of the relative shift of R and R' lines they require a large variation of the trigonal field with pressure. This is in contrast with our conclusion that the trigonal field does not change significantly with hydrostatic pressure. Therefore, the assumed interaction of Ma et al.¹⁶ requires a reconsideration. In fact, V_{trig} does not couple the 2E and 2T_1 states to the first order.^{1,5} Significant configuration interaction is through 2T_2 and is therefore of second order in perturbation. Ma et al.¹⁶ require a fairly strong interaction between 2E and 2T_1 states

and, further, it needs to increase rapidly with pressure. We feel that such an effective interaction actually emerges because of increased mixing of oxygen p orbitals with that of Cr^{3+} d orbitals.³³ Such a mixing is expected to be mainly responsible for the removal of accidental degeneracy of 2E and 2T_1 levels which exists within first order perturbative treatment with d orbitals.⁵ The same could well be the cause of disagreement of observed sensitivity of R' lines¹⁹ with crystal field theoretical predictions.⁹

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TABLE I: Variation in R_1 - R_2 splitting due to observed¹⁷ changes of the trigonal field. Eq. (1) gives the upper and Eq. (2) gives the lower bound.

Pressure (kbar)	Upper bound (cm^{-1})	Lower bound (cm^{-1})
0	29.6	29.6
↓		
75	29.6	29.6
92	33.4	32.4
102	36.4	34.6
120	39.7	37.0